9. *An Update to NRLXRF and NBSGSC – Fundamental Parameters in X-Ray Fluorescence Spectrometry*

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Objective: To bring up to date the landmark X-ray fluorescence (XRF) fundamental parameters computer programs NRLXRF (1978) and NBSGSC (1985). To update atomic parameters published since 1985 and to include an improved calculation of the spectrum from an X-ray tube. To publish this new database, to allow its critical evaluation and use.

Problem: XRF analysts apply fundamental parameter (FP) software to improve accuracy when they have few calibration standards. The programs NRLXRF and NBSGSC have served this purpose for over 15 years and still are requested, even though their algorithms, data files, and programming codes are significantly dated, limiting important applications, especially for custom spectrometer development. Commercial software developers have not adopted a standardized database form for the fundamental parameters and do not provide source codes that can easily be modified for research.

Approach: The fundamental parameters method relies on the use of equations that express the intensity of X-ray emission in terms of parameters that are independent of a particular sample. These parameters fall into two categories: instrument parameters and atomic parameters. Instrument parameters can be measured or are known *a priori*. The remaining parameters are associated with the elements of which the sample is composed and describe the X-ray properties of these elements. The properties of the elements together with the elemental composition of the sample can be used to compute the expected X-ray emission of the sample. The computations can be iterated to determine the composition of an unknown sample. The accuracy of the atomic parameters is crucial to the accuracy of the FP method. In particular, X-ray absorption cross-sections contribute directly to the quality of the results. Other parameters, e.g., Coster-Kronig transition probabilities, produce smaller effects and high accuracy is not required. However, the more accurate the parameters, the more useful the calculations will be and the greater the accuracy that can be achieved.

Table 1. Fundamental parameters required for calculations in XRF. Parameters are needed for each element in a sample

Atomic number	Photoabsorption cross-section
Atomic weight	Coherent scattering cross-section
Pure element density	Incoherent scattering cross-section
X-ray absorption edges: Energy Jump ratio Fluorescence yield	Coster-Kronig transition probability: X-ray emission lines Energy Relative intensity

The authors undertook to produce a consistent set of parameters optimized for FP calculations using values available in the literature. The required parameters are given in Table 1. The newer and more complete IUPAC notation is used for X-ray emission lines. The calculation of spectra from X-ray tubes was based on recent work in electron microprobe analysis. The fast and versatile FP algorithm from NRLXRF was used because it handles mixtures of compounds and particulate samples rather than simple elemental compositions and it can be extended to multilayer samples by using the analytical solutions to Sherman's equations derived by De Boer.

Results and Future Plans: The results of this work, in the form of both a database and computer source code, will be made available to the public and to commercial XRF software developers. At present, the computer codes are nearly ready to perform the first FP calculations of intensity from samples to verify the output of the code and check for improvements in accuracy with the new parameters. Modifications for particulate and multilayer samples are planned. Finally, a graphical user interface will be added to the program as time permits.